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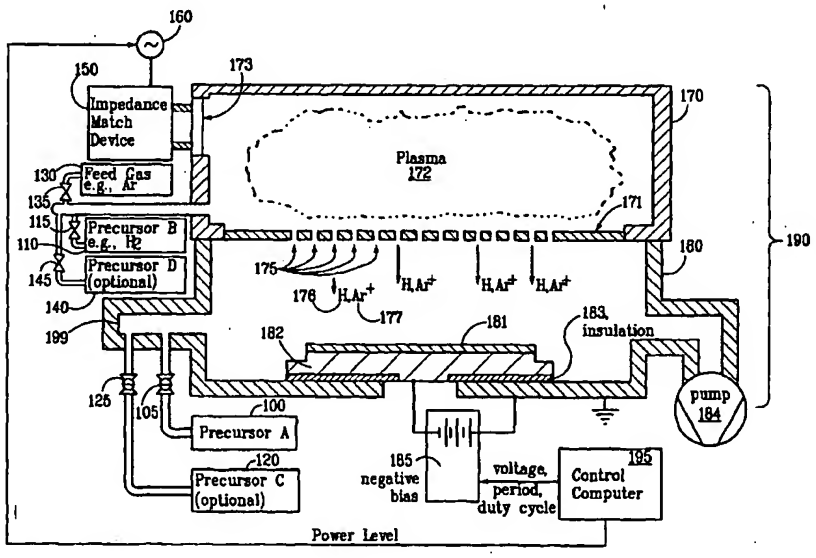
(54) Title: SYSTEM AND METHOD FOR MODULATED ION-INDUCED ATOMIC LAYER DEPOSITION (MII-ALD)



(57) Abstract: The present invention relates to an enhanced sequential or non-sequential atomic layer deposition (ALD) apparatus and technique suitable for deposition of barrier layers, adhesion layers, seed layers, low dielectric constant (low-k) films, high dielectric constant (high-k) films, and other conductive, semi-conductive, and non-conductive films. This is accomplished by providing a non-thermal or non-pyrolytic means of triggering the deposition reaction; providing a means of depositing a purer film of higher density at lower temperatures; providing a means of modulating the deposition sequence and hence the overall process rate; and providing a means of improved radical (176) generation and delivery.

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Specification

Cross-Reference to Related Applications

This application claims the benefit of U.S. Provisional Application Nos. 60/251,795, and 60/254,280, both filed December 6, 2000, as well as U.S. Utility Application Nos. 09/812,285, 09/812,352, and 09/812,486, all filed March 19, 2001, and U.S. Utility Application No. 09/854,092, filed May 10, 2001.

Background of the Invention

The present invention relates generally to the field of advanced thin film deposition methods commonly used in the semiconductor, data storage, flat panel display, as well as allied or other industries. More particularly, the present invention relates to an enhanced sequential or non-sequential atomic layer deposition (ALD) apparatus and technique suitable for deposition of barrier layers, adhesion layers, seed layers, low dielectric constant (low-k) films, high dielectric constant (high-k) films, and other conductive, semi-conductive, and non-conductive thin films.

The disadvantages of conventional ALD are additionally discussed in a copending application with the same assignee entitled "Method and Apparatus for Improved Temperature Control in Atomic Layer Deposition", which is hereby incorporated by reference in its entirety and may be found as copending provisional, Application No. 09/854,092.

Brief Description of the Prior Art

As integrated circuit (IC) dimensions shrink and the aspect ratios of the resulting features increase, the ability to deposit conformal, ultra-thin films on the sides and bottoms of high aspect ratio trenches and vias becomes increasingly important. These conformal, ultra-thin films are typically used as "liner" material to enhance adhesion, prevent inter-diffusion and/or chemical reaction between the underlying dielectric and the overlying metal, and promote the deposition of a subsequent film.

In addition, decreasing device dimensions and increasing device densities has necessitated the transition from traditional CVD tungsten plug and aluminum interconnect technology to copper interconnect technology. This transition is driven by both the increasing impact of the RC interconnect delay on device speed and by the electromigration (i.e., the mass transport of metal due to momentum transfer between conducting electrons and diffusing metal atoms, thereby affecting reliability) limitations of aluminum based conductors for sub 0.25 μm device generations. Copper is preferred due to its lower resistivity and higher (greater than 10 times) electromigration resistance as compared to aluminum. A single or dual damascene copper metallization scheme is used since it eliminates the need for copper etching and reduces the number of integration steps required. However, the burden now shifts to the metal deposition step(s) as the copper must fill predefined high aspect ratio trenches and/or vias in the dielectric. Electroplating has emerged as the copper fill technique of choice due to its low deposition temperature, high deposition rate, and potential low manufacturing cost.

Two major challenges exist for copper wiring technology: the barrier and seed layers. Copper can diffuse readily into silicon and most dielectrics. This diffusion may lead to electrical leakage between metal wires and poor device performance. An encapsulating barrier layer is needed to isolate the copper from the surrounding material (e.g., dielectric or Si), thus preventing copper diffusion into and/or reaction with the underlying material (e.g. dielectric or Si). In addition, the barrier layer also serves as the adhesion or glue layer between the patterned dielectric trench or via and the copper used to fill it. The dielectric material can be a low dielectric constant, i.e. low-k material (used to reduce inter- and intra-line capacitance and cross-talk) which typically suffers from poorer adhesion characteristics and lower thermal stability than traditional oxide insulators. Consequently, this places more stringent requirements on the barrier material and deposition method. An inferior adhesion layer will, for example, lead to delamination at either the barrier-to-dielectric or barrier–to-copper interfaces during any subsequent anneal and/or chemical mechanical planarization (CMP) processing steps leading to degradation in device performance and reliability. Ideally, the barrier layer should be thin, conformal, defect free, and of low resistivity so as to not compromise the conductance of the copper metal interconnect structure.

In addition, electroplating fill requires a copper seed layer, which serves to both carry the plating current and act as the nucleation layer. The preferred seed layer should be smooth, continuous, of high purity, and have good step coverage with low overhang. A discontinuity in the seed layer will

lead to sidewall voiding, while gross overhang will lead to pinch-off and the formation of top voids.

Both the barrier and seed layers which are critical to successful implementation of copper interconnects require a means of depositing high purity, conformal, ultra-thin films at low substrate temperatures.

Physical vapor deposition (PVD) or sputtering has been adopted as the preferred method of choice for depositing conductor films used in IC manufacturing. This choice has been primarily driven by the low cost, simple sputtering approach whereby relatively pure elemental or compound materials can be deposited at relatively low substrate temperatures. For example, refractory based metals and metal compounds such as tantalum (Ta), tantalum nitride (TaN_x), other tantalum containing compounds, tungsten (W), tungsten nitride (WN_x), and other tungsten containing compounds which are used as barrier/adhesion layers can be sputter deposited with the substrate at or near room temperature. However, as device geometries have decreased, the step coverage limitations of PVD have increasingly become an issue since it is inherently a line-of-sight process. This limits the total number of atoms or molecules which can be delivered into the patterned trench or via. As a result, PVD is unable to deposit thin continuous films of adequate thickness to coat the sides and bottoms of high aspect ratio trenches and vias. Moreover, medium/high-density plasma and ionized PVD sources developed to address the more aggressive device structures are still not adequate and are now of such complexity that cost and reliability have become serious concerns.

Chemical vapor deposition (CVD) processes offer improved step coverage since CVD processes can be tailored to provide conformal films. Conformality ensures the deposited films match the shape of the underlying substrate, and the film thickness inside the feature is uniform and equivalent to the thickness outside the feature. Unfortunately, CVD requires comparatively high deposition temperatures, suffers from high impurity concentrations, which impact film integrity, and have higher cost-of-ownership due to long nucleation times and poor precursor gas utilization efficiency. Following the tantalum containing barrier example, CVD Ta and TaN films require substrate temperatures ranging from 500 °C to over 800 °C and suffer from impurity concentrations (typically of carbon and oxygen) ranging from several to tens of atomic % concentration. This generally leads to high film resistivities (up to several orders of magnitude higher than PVD), and other degradation in film performance. These deposition temperatures and impurity concentrations make CVD Ta and TaN unusable for IC manufacturing, in particular for copper metallization and low-k integration.

Chen et al. ("Low temperature plasma-assisted chemical vapor deposition of tantalum nitride from tantalum pentabromide for copper metallization", J. Vac. Sci. Technol. B 17(1), pp. 182-185 (1999); and "Low temperature plasma-promoted chemical vapor deposition of tantalum from tantalum pentabromide for copper metallization", J. Vac. Sci. Technol. B 16(5), pp. 2887-2890 (1998)) have demonstrated a plasma-assisted (PACVD) or plasma-enhanced (PECVD) CVD approach using tantalum pentabromide ($TaBr_5$) as the precursor gas to reduce the deposition temperature. Ta and

TaN_x films were deposited from 350 °C to 450 °C and contained 2.5 to 3 atomic % concentration of bromine. Although the deposition temperature has been reduced by increased fragmentation (and hence increased reactivity) of the precursor gases in the gas-phase via a plasma, the same fragmentation leads to the deposition of unwanted impurities. Gas-phase fragmentation of the precursor into both desired and undesired species inherently limits the efficacy of this approach.

Recently, atomic layer chemical vapor deposition (AL-CVD) or atomic layer deposition (ALD) has been proposed as an alternative method to CVD for depositing conformal, ultra-thin films at comparatively lower temperatures. ALD is similar to CVD except that the substrate is sequentially exposed to one reactant at a time. Conceptually, it is a simple process: a first reactant is introduced onto a heated substrate whereby it forms a monolayer on the surface of the substrate. Excess reactant is pumped out. Next a second reactant is introduced and reacts with the first reactant to form a monolayer of the desired film via a self-limiting surface reaction. The process is self-limiting since the deposition reaction halts once the initially adsorbed (physi- or chemi-sorbed) monolayer of the first reactant has fully reacted with the second reactant. Finally, the excess second reactant is evacuated. The above sequence of events comprises one deposition cycle. The desired film thickness is obtained by repeating the deposition cycle the required number of times.

In practice, ALD is complicated by the painstaking selection of a process temperature setpoint wherein both: 1) at least one of the reactants

sufficiently adsorbs to a monolayer and 2) the surface deposition reaction can occur with adequate growth rate and film purity. If the substrate temperature needed for the deposition reaction is too high, desorption or decomposition of the first adsorbed reactant occurs, thereby eliminating the layer-by-layer process. If the temperature is too low, the deposition reaction may be incomplete (i.e., very slow), not occur at all, or lead to poor film quality (e.g., high resistivity and/or high impurity content). Since the ALD process is entirely thermal, selection of available precursors (i.e., reactants) that fit the temperature window becomes difficult and sometimes unattainable. Due to the above-mentioned temperature related problems, ALD has been typically limited to the deposition of semiconductors and insulators as opposed to metals. ALD of metals has been confined to the use of metal halide precursors. However, halides (e.g., Cl, F, Br) are corrosive and can create reliability issues in metal interconnects.

Continuing with the TaN example, ALD of TaN films is confined to a narrow temperature window of 400 °C to 500 °C, generally occurs with a maximum deposition rate of 0.2 Å/cycle, and can contain up to several atomic percent of impurities including chlorine and oxygen. Chlorine is a corrosive, can attack copper, and lead to reliability concerns. The above process is unsuitable for copper metallization and low-k integration due to the high deposition temperature, slow deposition rate, and chlorine impurity incorporation.

In conventional ALD of metal films, gaseous hydrogen (H_2) or elemental zinc (Zn) is often cited as the second reactant. These reactants are

chosen since they act as a reducing agent to bring the metal atom contained in the first reactant to the desired oxidation state in order to deposit the end film. Gaseous, diatomic hydrogen (H_2) is an inefficient reducing agent due to its chemical stability, and elemental zinc has low volatility (e.g., it is very difficult to deliver sufficient amounts of Zn vapor to the substrate) and is generally incompatible with IC manufacturing. Unfortunately, due to the temperature conflicts that plague the ALD method and lack of kinetically favorable second reactant, serious compromises in process performance result.

In order to address the limitations of traditional thermal or pyrolytic ALD, radical enhanced atomic layer deposition (REALD, US Patent 5,916,365) or plasma-enhanced atomic layer deposition has been proposed whereby a downstream radio-frequency (RF) glow discharge is used to dissociate the second reactant to form more reactive radical species which drives the reaction at lower substrate temperatures. Using such a technique, Ta ALD films have been deposited at 0.16 to 0.5 Å/cycle at 25 °C, and up to approximately 1.67 Å/cycle at 250 °C to 450 °C. Although REALD results in a lower operating substrate temperature than all the aforementioned techniques, the process still suffers from several significant drawbacks. Higher temperatures must still be used to generate appreciable deposition rates. Such temperatures are still too high for some films of significant interest in IC manufacturing such as polymer-based low-k dielectrics that are stable up to temperatures of only 200 °C or less. REALD remains a thermal or pyrolytic process similar to ALD and even CVD since the substrate

temperature provides the required activation energy for the process and is therefore the primary control means for driving the deposition reaction.

In addition, Ta films deposited using REALD still contain chlorine as well as oxygen impurities, and are of low density. A low density or porous film leads to a poor barrier against copper diffusion since copper atoms and ions have more pathways to traverse the barrier material. Moreover, a porous or under-dense film has lower chemical stability and can react undesirably with overlying or underlying films, or with exposure to gases commonly used in IC manufacturing processes.

Another limitation of REALD is that the radical generation and delivery is inefficient and undesirable. RF plasma generation of radicals used as the second reactant such as atomic H is not as efficient as microwave plasma due to the enhanced efficiency of microwave energy transfer to electrons used to sustain and dissociate reactants introduced in the plasma. Furthermore, having a downstream configuration whereby the radical generating plasma is contained in a separate vessel located remotely from the main chamber where the substrate is situated and using a small aperture to introduce the radicals from the remote plasma vessel to the main chamber body significantly decreases the efficiency of transport of the second radical reactant. Both gas-phase and wall recombination will reduce the flux of desired radicals that can reach the substrate. In the case of atomic H, these recombination pathways will lead to the formation of diatomic H_2, a far less effective reducing agent. If the plasma used to generate the radicals was

placed directly over the substrate, then the deposition of unwanted impurities and particles can occur similarly to the case of plasma-assisted CVD.

Finally, ALD (or any derivative such as REALD) is fundamentally slow since it relies on a sequential process whereby each deposition cycle is comprised of at least two separate reactant flow and evacuation steps, which can occur on the order of minutes with conventional valve and chamber technology. Significant improvements resulting in faster ALD are needed to make it more suitable for commercial IC manufacturing.

Brief Description of The Drawings

Figure 1 is a schematic of a deposition system suitable for modulated ion-induced atomic layer deposition (MII-ALD).

Figure 2A depicts a timing sequence for an improved ALD method incorporating periodic exposure of the substrate to ions.

Figure 2B is another timing sequence for an improved ALD method incorporating periodic exposure of the substrate to ions.

Figure 3A shows the MII-ALD method utilizing ion flux modulation to vary the substrate exposure to ions.

Figure 3B shows the timing of the MII-ALD method utilizing ion energy modulation to vary the substrate exposure to ions by varying the substrate bias.

Figures 4A-F show methods of modulating the MII-ALD process.

Figure 5 shows an electrostatic chuck (ESC) system suitable for modulating the ion energy in the MII-ALD process: a) in topological form; and, b) as an equivalent electrical circuit.

Summary and Detailed Description of the Invention

The present invention relates to methods and apparatuses useable for the deposition of conformal solid thin films of one or more elements at low temperature. More particularly, the present invention relates to an enhanced sequential or, more preferably, non-sequential atomic layer deposition apparatus and technique suitable for deposition of barrier layers, adhesion layers, seed layers, and low dielectric constant (low-k) films, high dielectric constant (high-k) films, and other conductive, semi-conductive, and non-conductive thin films.

More specifically, the present invention resolves the previously presented problems encountered in the prior art (e.g., REALD) by 1) providing a non-thermal or non-pyrolytic means of triggering the deposition reaction; 2) providing a means of depositing a purer film of higher density at lower temperatures; 3) providing a faster and more efficient means of modulating the deposition sequence and hence the overall process rate resulting in an improved deposition method; and, 4) providing a means of improved radical generation and delivery.

Improvements to ALD processing, e.g., the REALD mentioned previously, remain "thermal" or "pyrolytic" processes since the substrate temperature provides the required activation energy and is the primary control knob for driving the deposition reaction. Alternatively, we propose a novel approach by providing the required activation energy from a "non-thermal" source. In particular, we propose driving the deposition reaction primarily via substrate exposure to impinging ions wherein the ions are used

to deliver the necessary activation energy to the near surface atoms and adsorbed reactant(s) via collision cascades.

Conventional deposition processes used in the semiconductor industry (including ALD) typically deposit materials at temperatures in the range of 300-600 °C. The deposition method described herein can be effected at much lower temperatures, in practice as low as 25 °C or below. Note that this process is ion-triggered (i.e., ion-induced) as opposed to ion-assisted in that deposition will not generally occur without ion bombardment since ions are used as the primary means of providing the activation energy required for deposition. A primary benefit of ion-induced processing is the deposition of higher density films of superior purity and adhesion properties. This result occurs due to ion bombardment induced densification.

Figure 1 illustrates a deposition system suitable for modulated ion-induced atomic layer deposition (MII-ALD). The invention described herein also incorporates a means of modulating the exposure of the substrate to ions. By modulating 1) the ion flux; 2) the energy of the ions striking the substrate; or a combination of (1) and (2), the deposition reaction can be precisely toggled "on" or "off". If the ion flux or energy is at a "low" state, then no deposition results or deposition occurs so slowly that essentially no deposition results. If the impinging ion flux or energy is at a "high" state, then deposition occurs. Since the substrate (which may be a "bare" substrate, e.g., a silicon wafer before any films have been deposited, or it may be a substrate which may already have had one or more films deposited on its surface) **181** is preferably maintained at a low substrate temperature, the first

and second reactants do not thermally react with any appreciable rate or do not react at all. Instead, the deposition reaction only takes place when either the ion flux or ion energy is toggled to a suitable "high state". The desired film thickness is built up by repeating the ion pulses (either of flux or energy) the required number of cycles. Furthermore, since modulation of the ion flux or ion energy can occur on a much faster time scale (KHz range) than the conventional valve and pump technology used in ALD (up to minutes per cycle), this deposition method is more suitable for commercial IC manufacturing. This method shall be referred to herein as modulated ion-induced atomic layer deposition (MII-ALD).

In addition, the present invention also improves upon the prior art by employing a microwave generated plasma **172** substantially contained in the main chamber body **190** that is isolated via a distribution showerhead **171** comprised of a series or array of apertures **175** which resolves the issues of radical generation and delivery, while preventing gas-phase precursor cracking (i.e., fragmentation or breaking down the precursor gas into its constituent elements) and impurity and/or particle generation directly above the wafer **181**. The plasma is contained within the plasma source chamber **170** itself and is not in direct communication with the substrate **181**. In MII-ALD, the same plasma is used to generate both ions **177** (used to drive the surface reactions) and radicals **176** (used as the second reactant), but is isolated from the first reactant **100** which typically contains both the principal element(s) desired in the end film, but also unwanted impurity containing byproducts. Therefore, primarily only the radicals **176** and ions **177** are able to travel

through the showerhead apertures **175**. The plasma **172** is essentially contained within the plasma source chamber and does not intermingle with the precursor gases **100, 120**.

The present invention utilizes ion imparted kinetic energy transfer rather than thermal energy (e.g., REALD, ALD, PECVD, CVD, etc.) to drive the deposition reaction. Since temperature can be used as a secondary control variable, with this enhancement films can be deposited using MII-ALD at arbitrarily low substrate temperatures (generally less than 350 °C). In particular, films can be deposited at or near room temperature (i.e., 25°C) or below.

The system of Figure 1 contains a substantially enclosed plasma source chamber **170** located in substantial communication with or, more preferably, substantially within a main chamber body **190**. The plasma **172** is used to dissociate feed gases **130, 110** to generate both ions **177** and radicals **176**. Typical feed gases **130** used for ion generation include, but are not restricted to Ar, Kr, Ne, and Xe. Typical feed gases **110** (e.g., precursor B) used for radical generation include, but are not restricted to H_2, O_2, N_2, NH_3, and H_20 vapor. The ions **177** are used to deliver the energy needed to drive surface reactions between the first adsorbed reactant and the generated radicals **176**. Inductively coupled RF (e.g., 400 KHz, 2 MHz, 13.56 MHz, etc.) power **160** can be used to generate the plasma via solenoidal coils located within or outside of the plasma chamber (not shown in Figure 1). More preferably, microwave (e.g., generally 2.45 GHz or higher frequencies) power **160** is coupled to the plasma source chamber **170** via a suitable means such as a waveguide or

coaxial cable. Microwave energy can be more efficiently transferred to ionizing electrons, leading to higher ionization fractions. This is of particular importance in the generation of radicals **176** (i.e., a chemical fragment of a larger molecule) such as atomic hydrogen, or any of a number of other reactive groups such as nitrogen atoms (N), oxygen atoms (O), OH molecules, or NH molecules, or a combination thereof. These radicals serve as the second reactant. Microwave or radio-frequency (RF) power **160** is coupled to the plasma **172** via a dielectric material **173**, which may be a dielectric window such as quartz embedded in the chamber wall, or it may be empty space in the case of a microwave or RF antenna located within the plasma chamber.

In addition, a distribution showerhead **171**, containing a series or array of apertures **175** through which ions **177** and radicals **176** are delivered to the substrate **181**, isolates the main process chamber **180** from the plasma source chamber **170**. A pressure drop (for example, a 5 or 10 times decrease in pressure, with the main processing chamber **180** being at the lower pressure) is thereby created between the plasma source chamber **170** and the main processing chamber **180** to project the ions **177** and radicals **176** to the substrate **181** via the distribution showerhead **171**. The plasma source chamber **170** is generally of comparable diameter to the main chamber body **190** to enable large area exposure of the sample. The size, aspect ratio, and distribution of the showerhead apertures **175** can be optimized to provide uniform exposure of the substrate **181** and the desired ion **177** to radical **176** ratio. The distance between this showerhead **171** and the substrate **181** may vary depending on the application. For the processing of wafers in the IC

industry, this distance is preferably at most two wafer diameters and more preferably less than or equal to one half a wafer diameter.

Having a substantially enclosed plasma generation chamber **170** situated within the main chamber **190** allows efficient and uniform delivery of ions **177** and radicals **176** to the substrate **181**. In addition, by isolating the plasma **172** from the main chamber **180** prevents gas-phase cracking of the first reactant **100** (e.g., precursor A), which is introduced directly to the main processing chamber **180** via a gas distribution manifold **199**. Precursor A **100** may be any one or more of a series of gaseous compounds used for depositing semiconductors, insulators, metals or the like that are well-known in the art (e.g, PDEAT (pentakis(diethylamido)tantalum), PEMAT (pentakis(ethylmethylamido)tantalum), $TaBr_5$, $TaCl_5$, TBTDET (t-butylimino tris(diethylamino) tantalum), $TiCl_4$, TDMAT (tetrakis(dimethylamido)titanium), TDEAT (tetrakis(diethylamino)titanium), CuCl, Cupraselect® ((Trimethylvinylsilyl)hexafluoroacetylacetonato Copper I), $W(CO)_6$, WF_6, etc.) and examples will be further discussed herein. Finally, the ion/radical distribution showerhead **171** shields the dielectric wall **173** adjacent to the supplied RF or microwave power **160** against being coated by precursor A **100** during processing which can degrade power transfer to the plasma **172** in processing systems found in the prior art. This is of particular importance in the case of deposition of conductors whereby if the dielectric **173** is fully exposed to the metal containing first reactant **100** (e.g., precursor A) and if the plasma **172** was directly generated within the main chamber **190** without the use of an isolating distribution showerhead **171**, then metal

deposition onto the dielectric **173** will eventually shield out RF or microwave power **160** from the plasma **172** such that the plasma **172** will extinguish.

Figure 2A depicts a sequence for an improved ALD method incorporating periodic exposure of the substrate to ions. In this variant of the method, ion exposure **230** begins with the introduction of the second precursor **220** (especially when plasma generated radicals **176** are used as the second precursor or reactant). This figure illustrates one embodiment of MII-ALD utilizing the apparatus described in Figure 1. This results in an enhanced sequential ALD process as follows:

1) First exposure **200**: The substrate **181** is exposed to a first gaseous reactant **100** (e.g., precursor A), allowing a monolayer of the reactant to form on the surface. The substrate **181** may be at any temperature below the decomposition temperature of the first gaseous reactant although it is preferable for the temperature to generally be less than approximately 350 °C.

2) First evacuation **210**: The excess reactant **100** is removed by evacuating **214** the chamber **180** with a vacuum pump **184**.

3) Second exposure **220**: Unlike conventional ALD, the substrate **181** is simultaneously exposed to ions **177** and a second gaseous reactant (e.g., microwave or RF plasma generated radicals **176**) during this step with the substrate **181** (e.g., wafer) biased to a negative potential V_{bias} **185**. Microwave or RF power **160** is supplied into the plasma chamber **170** to generate both the ions **177** (e.g., argon-ion (Ar^+)) and radicals **176** (e.g., H atoms). The ions will strike the wafer **181** with an energy approximately equal to $(e|V_{bias}| + e|V_p|)$ where V_p is the plasma **172** potential (typically 10V to 20V). V_{bias} (-20V to -

500V) is typically chosen to be greater than V_p in magnitude, and is used to control the ion **177** energy. With the activation energy now primarily supplied by ions **177** instead of thermal energy, the first and second (chemi- or physi-sorbed) reactants react via an ion-induced surface reaction to produce a solid thin monolayer of the desired film at a reduced substrate temperature below conventional ALD. The deposition reaction between the first and second reactants is self-limiting in that the reaction between them terminates after the initial monolayer of the first reactant **100** is consumed.

4) Second evacuation **210**: The excess second reactant is removed by again evacuating **216** the chamber **180** with the vacuum pump **184**.

5) Repeat: The desired film thickness is built up by repeating the entire process cycle (steps 1-4) many times.

Additional precursor gases (e.g., **120, 140**) may be introduced and evacuated as required for a given process to create tailored films of varying compositions or materials. As an example, an optional exposure may occur in the case of a compound barrier of varying composition. For example, a TaN_x/Ta film stack is of interest in copper technology since TaN_x prevents fluorine attack from the underlying fluorinated low-k dielectrics, whereas the Ta promotes better adhesion and crystallographic orientation for the overlying copper seed layer. The TaN_x film may be deposited using a tantalum containing precursor (e.g., $TaCl_5$, PEMAT, PDEAT, TBTDET) as the first reactant **100** (precursor A) and a mixture of atomic hydrogen and atomic nitrogen (i.e. flowing a mixture of H_2 and N_2 into the plasma source **172**) as the second reactant to produce a TaN_x film. Simultaneous ion exposure is

used to drive the deposition reaction. Next a Ta film may be deposited in a similar fashion by using atomic hydrogen (as opposed to a mixture of atomic hydrogen and nitrogen) as the second reactant. An example of a tailored film stack of differing materials can be the subsequent deposition of a copper layer over the TaN_x /Ta bi-layer via the use of a copper containing organometallic (e.g., Cu(TMVS)(hfac) or (Trimethylvinylsilyl)hexafluoroacetylacetonato Copper I, also known by the trade name CupraSelect®, available from Schumacher, a unit of Air Products and Chemicals, Inc., 1969 Palomar Oaks Way, Carlsbad, CA 92009) or inorganic precursor (e.g. CuCl) shown as precursor C **120** in Figure 1. The copper layer can serve as the seed layer for subsequent electroless or electroplating deposition.

A variant of the method shown in Figure 2A is illustrated in Figure 2B where ion exposure is initiated after the second reactant exposure. Figure 2B depicts a sequence for an improved ALD method incorporating periodic exposure of the substrate **181** to ions **177**. In this variant of the method, ion exposure **280** begins with the evacuation **250** of the second precursor **256** (especially when the second precursor or reactant is not subjected to a plasma). Typically, this is the case where the second precursor or reactant is not a plasma-generated radical.

In the previous embodiments of MII-ALD, although the deposition temperature can be lowered significantly, the first and second reactants are still sequentially introduced into the main process chamber **180**, and hence will still be a slow process. It is of particular interest to eliminate or replace

the time-consuming flow-evacuation-flow-evacuation sequential nature of the process.

In the preferred embodiment of the MII-ALD process, a substrate **181** heated (e.g., to a low temperature of less than or equal to 350 °C) or unheated is simultaneously exposed to a first reactant and a second reactant, and subjected to modulated ion **177** exposure. By modulating 1) the ion flux (i.e. the number of ions hitting the substrate per unit area per unit time); 2) the energy of the ions striking the substrate; or a combination of (1) and (2), the deposition reaction can be precisely toggled "on" or "off". Since the substrate **181** is preferably maintained at a low substrate temperature, the first and second reactants do not thermally react with any appreciable rate or do not react at all when the ion flux or energy is toggled to a "low" state. Instead, the deposition reaction only takes place when either the ion flux or ion energy is toggled to a suitable "high state". Ion flux or energy modulation can vary generally from 0.1 Hz to 20 MHz, preferably from 0.01 KHz to 10 KHz. During deposition, the main process chamber **180** pressure can be maintained in the range of generally 10^{2} to 10^{-7} torr, more preferably from 10^{1} to 10^{-4} torr, depending on the chemistry involved. The desired film thickness is attained via exposure of the substrate to the suitable number of modulated ion flux or energy pulse cycles. This MII-ALD scheme results in a "continuous" deposition process that is significantly faster than conventional sequential ALD since the two, slow evacuation steps (up to minutes) are eliminated and replaced by the faster (KHz range or above) ion modulation steps. The

modulation can be either of the ion flux via the plasma power or of the ion energy via an applied periodic wafer bias.

The MII-ALD method utilizing ion flux modulation to control the deposition cycle is illustrated conceptually in Figure 3A, with the flux modulation scheme described more explicitly in Figures 4A and 4C. Figure 3A depicts the MII-ALD method utilizing ion flux modulation **320** to vary the substrate **181** exposure to ions **177**. Note that the second reactant **310**, e.g., radicals, is synchronized with the ion flux via **320** plasma power modulation, causing a periodic exposure of the substrate to ions and radicals. Varying the power **160** delivered to the plasma **172** can vary the ion flux from little or none to maximum ion production. Plasma power modulation can take the form of variations in frequency (periodicity), magnitude, and duty-cycle. Increasing plasma power **160** leads to increasing plasma **172**, and hence, increased ion **177** density. Since the deposition process is ion-induced, having little or no ion bombardment will essentially stop the deposition process, whereas increased ion bombardment will cause deposition to occur. A constant wafer bias **185** (DC in Figure 4C or RF in Figure 4A) is applied to define the ion energy of the modulated ion flux in this embodiment and is chosen to be sufficiently high so that ion-induced surface reactions can occur. Note that in this embodiment since the plasma (either RF or preferably microwave) power **160** is used to generate both ions **177** and radicals **176**, the second reactant (e.g., radicals) flux **310** is synchronized with the ion flux **320** pulses. The radical feed gas **110** (H_2 for example) flow, however, does not

change. Instead, the radical flux **310** (e.g., fraction of H_2 which is converted to atomic H) is modulated.

Alternatively, subjecting the substrate **181** to a non-constant wafer voltage bias **185** can vary the incoming ion energy at a fixed plasma power **160** (i.e., ion flux). This preferred embodiment of MII-ALD is illustrated conceptually in Figures 3B, and more explicitly in Figures 4B and 4D. Figure 3B shows the MII-ALD method utilizing ion energy modulation **350** to vary the substrate **181** exposure to ions **177** by varying the substrate bias **185**. The applied bias **185** can take the form of variations in frequency (periodicity), magnitude, and duty-cycle. A DC as shown in Figure 4D or RF (e.g., 400 kHz, 2 MHz, 13.56 MHz, etc.) as shown in Figure 4B power supply can be used. When the wafer potential is "low" (e.g., near or at zero with respect to ground), the incoming ions **177** do not have enough energy to induce surface deposition reactions. When the wafer **181** potential is "high" (e.g., at a significant negative potential relative to ground), the incoming ions **177** will have the necessary energy to induce surface deposition reactions via collision cascades. In such a fashion, the deposition can be turned "on" or "off" by modulating the wafer bias voltage **185**, and hence the impinging ion **177** energy. Typical wafer voltages can range from generally –20 V to –1000 V, but preferably in the –25 V to –500 V range, and more preferably in the –50 V to –350 V range during deposition. The bias voltage **185** is coupled to the wafer via the pedestal **182**. Preferably, the substrate pedestal **182** is an electrostatic chuck (ESC) to provide efficient coupling of bias voltage to the substrate. The ESC is situated in the main processing chamber **180** and can be

cooled via a fluid coolant (preferably a liquid coolant) and/or heated (e.g., resistively) to manipulate the substrate temperature.

As illustrated in Figure 5 for the case of an applied DC bias, the preferred electrostatic chuck is a "coulombic" ESC **500** (bulk resistivity generally greater than 10^{13} ohm-cm) rather than one whose bulk material effects are dominated by the Johnson-Rahbek (JR) effect (bulk resistivity between 10^{8} and 10^{12} ohm-cm). Typically, the substrate potential is a complex function of the voltage of the electrostatic "chucking" electrodes if these voltages are established relative to a reference potential, but is simplified in the case of "coulombic" (non-JR) ESC. However, if the power supply **510** that powers the ESC **500** is truly floating, i.e., the entire system has a high impedance to the chamber **180** potential (usually ground) including the means of supplying power, then the substrate potential can be arbitrary. In particular, if the ESC power supply **510** is also center-tapped **518**, then the wafer potential can be established by connecting the center tap **518** to the output of a power amplifier **520**. This power amplifier can be controlled by a computer or a waveform generator **530** to periodically drop the substrate potential to a negative value for a certain period of time. It is desired to have independent control of the magnitude, frequency (periodicity), and duty cycle of this substrate bias pulse train. Such an ESC system is depicted in Figure 5, which shows an ESC system suitable for modulating the ion energy in the MII-ALD process: a) in topological form; and, b) as an equivalent electrical circuit.

The deposition rate is affected by the choice of the critical bias pulse train variables: the magnitude, frequency (periodicity), and duty cycle. Preferably, when the bias frequency is high (e.g., 100 Hz-10 KHz) with a short duty cycle (e.g., less than 30%), reducing the net, time-averaged current (which can cause substrate potential drift, de-chucking problems, or charge-induced device damage) while providing a charge relaxation period wherein the ion charges accumulated during ion exposure can redistribute and neutralize.

Once the deposition rate is calibrated for a particular recipe (Angstroms/cycle), the ability to accurately determine the film thickness by counting cycles is a further benefit of this modulation scheme. The higher the frequency, the finer the resolution of this critical deposition process performance metric.

Alternatively, the substrate potential can be modulated by imparting an induced DC bias to the substrate by applying RF power to the pedestal. Preferably, the RF power is coupled into the ESC electrodes. Figures 4A-F illustrate the preferred methods of modulating the MII-ALD process. In Figure 4A, an RF bias power $\mathbf{B}_2$ is applied to the substrate pedestal **182** imparting an induced DC bias $\mathbf{V}_2$ to the substrate while the plasma (either microwave or RF) power **400** is varied periodically between a high $\mathbf{P}_1$ and a low $\mathbf{P}_2$ power state. In Figure 4B, plasma (either microwave or RF) power **410** is constant $\mathbf{P}_1$ while an RF bias power, applied to the substrate pedestal **182**, is varied between a low $\mathbf{B}_1$ and a high $\mathbf{B}_2$ bias state ($\mathbf{V}_1$ and $\mathbf{V}_2$ are the DC offset or bias voltages resulting from the applied RF bias power). In Figure 4C, a

negative DC bias **425** is applied to the substrate pedestal **182** while the plasma (either microwave or RF) power **420** is varied periodically between a high P_1 and a low power P_2 state. In Figure 4D, plasma (either microwave or RF) power is constant **430** while a DC bias **435** applied to the substrate pedestal **182** is varied between a zero V_1 and a negative voltage state V_2. In Figure 4E, a mechanical shutter periodically occludes the ion source. All the while, the plasma power **440** (either microwave or RF) and substrate voltage **445** are held constant. In Figure 4F, a source area that is smaller than the substrate **181** is preferably used. In this case, plasma (either microwave or RF) power **450** is constant, a negative DC substrate bias **455** is constant, and the source and substrate **181** are moved relative to each other **457**, exposing only a portion of the substrate **181** at a time. The methods proposed in Figure 4B and Figure 4D, whereby the substrate bias is modulated at a constant plasma power **410, 430** and hence ion flux, are most preferred.

MII-ALD can be used to deposit dielectric, semiconducting, or metal films, among others, used in the semiconductor, data storage, flat panel display, and allied as well as other industries. In particular, the method and apparatus is suitable for the deposition of barrier layers, adhesion layers, seed layers, low dielectric constant (low-k) films, and high dielectric constant (high-k) films.

This process utilizes independent control over the three constituents of plasma – ions, atoms, and precursors. Decoupling these constituents offer improved control over the deposition process.

An added benefit of using MII-ALD is that with proper choice of the second reactant, selective ion-enhanced etching and removal of unwanted impurities can be performed. As an example, for many chemistries, the preferred second reactant is monatomic hydrogen (H) 176. Simultaneous energetic ion and reactive atomic H bombardment will cause selective removal of unwanted impurities (e.g., containing carbon, oxygen, fluorine, or chlorine) commonly associated with organometallic precursors (e.g., TBTDET, PEMAT, PDEAT, TDMAT, TDEAT), and proceed with removal rates superior to either chemical reaction (e.g., atomic H only) or physical sputtering (e.g., Ar ion only) alone. Impurities lead to high film resistivities, low film density, poor adhesion, and other deleterious film effects. Alternatively, in addition to atomic hydrogen, other reactive groups such as nitrogen atoms (N), oxygen atoms (O), OH molecules, or NH molecules, or a combination thereof may be employed.

From the description of the preferred embodiments of the process and apparatus set forth above, it is apparent to one of ordinary skill in the art that variations and additions to the embodiments can be made without departing from the principles of the present invention. As an example, chlorine, bromine, fluorine, oxygen, nitrogen, hydrogen, other reactants and/or radicals containing the aforementioned elements or a combination thereof, in conjunction with energetic ion bombardment, can be used to effect etching or material removal as opposed to deposition. This is of particular importance in the cleaning of native oxides of copper, aluminum, silicon, and other common conductor and semiconductor materials used in IC manufacturing.

Either the deposition or etching can be accomplished globally (as illustrated in the preceding embodiments) or may be chosen to be local to a controlled area (i.e., site-specific using a small, ion beam point or broad-beam source scanned or otherwise stepped across the substrate, exposing only a fraction of the substrate area at any given time).

System and Method for Modulated Ion-induced Atomic Layer Deposition (MII-ALD)

Claims

What is claimed is:

1. A sequential method for depositing a thin film onto a substrate in an evacuated chamber comprising:

introducing a first reactant gas into said chamber;

adsorption of at least one monolayer of said first reactant gas onto said substrate;

evacuation of excess said first reactant gas from said chamber

introduction of at least one ion generating feed gas into said chamber;

generating a plasma from said ion generating feed gas to form ions;

exposing said substrate to said ions;

modulating said ions; and

reacting said adsorbed monolayer of said first reactant gas with said ions to deposit said thin film.

2. The method of claim 1, wherein said ion modulation is modulated in a way selected from the group consisting of modulating an ion flux and modulating an ion energy.

3. The method of claim 1, further comprising maintaining said substrate at a temperature of between about 25 °C to 350 °C.

4. A system for ion-induced atomic layer deposition of a film onto a substrate, said system comprising:

a main chamber containing a plasma generation chamber for generating a plasma;

said main chamber also containing a deposition chamber for depositing said film on said substrate;

a distribution showerhead located between said plasma generation chamber and said deposition chamber;

said plasma generation chamber coupled to receive at least one feed gas to form said plasma for generation of ions;

said plasma generation chamber also coupled to receive at least one feed gas to react with said plasma for generation of radicals; and

said deposition chamber coupled to receive at least one precursor gas to react with said ions and said radicals to form said film on said substrate.

5. The system of claim 4, wherein said plasma generation chamber is in communication with a radio frequency energy source through a dielectric window.

6. The system of claim 5, wherein said distribution showerhead shields said dielectric window from being coated by said deposition chamber precursor gas.

7. The system of claim 4, wherein said plasma generation chamber is in communication with a microwave frequency energy source.

8. The system of claim 4 further comprising a substrate holder located in said deposition chamber, said substrate holder electrically biasing said substrate via a power supply.

9. The system of claim 8, wherein said power supply supplies a radio frequency power to induce said electrical bias on said substrate.

10. The system of claim 4, wherein said plasma generated in said plasma generation chamber does not intermingle with said deposition chamber precursor gas.

11. The system of claim 4, wherein said distribution showerhead is comprised of one or more apertures.

12. The system of claim 4, wherein a deposition reaction is controlled via ion-imparted kinetic energy.

13. The system of claim 4, further comprising a thermal heating element to control said film deposition on said substrate.

14. A system for generating a plasma for depositing a film onto a substrate, said system comprising:

a plasma generation source;

a plasma generation chamber coupled to said plasma generation source;

a deposition chamber; and

a distribution showerhead separating said plasma generation chamber from said deposition chamber.

15. The system of claim 14, wherein said plasma generation source may be modulated by a change selected from a group consisting of a change in frequency, a change in power magnitude, and a change in duty-cycle.

16. A sequential method for depositing a thin film onto a substrate in an evacuated chamber comprising:

introducing a first reactant gas into said chamber;

adsorption of at least one monolayer of said first reactant gas onto said substrate;

evacuation of excess said first reactant gas from said chamber

introduction of at least one ion generating feed gas into said chamber;

introduction of at least one radical generating feed gas into said chamber;

generating a plasma from said ion generating feed gas and said radical generating feed gas to form ions and radicals;

exposing said substrate to said ions and said radicals;

modulating said ions; and

reacting said adsorbed monolayer of said first reactant gas with said ions and said radicals to deposit said thin film.

17. The method of claim 16, wherein said method is repeated until the film achieves a desired thickness.

18. The method of claim 16, further comprising exposing said substrate to at least one additional reactant gas.

19. The method of claim 16, wherein said substrate is simultaneously exposed to said ions and said radicals

20. The method of claim 16, wherein said ion modulation is modulated in a way selected from the group consisting of modulating an ion flux and modulating an ion energy.

21. The method of claim 20, wherein modulation in said ion flux is modulated in a way selected from the group consisting of modulating a flow of said ion generating feed gas, modulating a power of said plasma, modulating said exposure to said ions, and modulating the relative movement between said plasma and said substrate.

22. The method of claim 16, further comprising maintaining said substrate at a temperature of between about 25 °C to 350 °C.

23. The method of claim 16, further comprising inducing an electrical bias on said substrate via a substrate pedestal on which said substrate rests.

24. The method of claim 23, wherein said pedestal is an electrostatic chuck (ESC) to provide coupling of said electrical bias to said substrate.

25. The method of claim 23, wherein said electrical bias is induced by a radio frequency power supply.

26. The method of claim 16, wherein an energy to generate said plasma is produced by a radio frequency source.

27. The method of claim 16, wherein an energy to generate said plasma is produced by a microwave source.

28. A method for depositing a thin film onto a substrate in an evacuated chamber comprising:

placing said substrate onto a substrate holder in a deposition chamber area;

introducing at least one ion generating feed gas into a plasma generation chamber area in communication with said deposition chamber area, but substantially isolated via a distribution showerhead comprised of one or more apertures located between said plasma generation chamber area and said deposition chamber area;

introducing at least one radical generating feed gas into said plasma generation chamber area;

generating a plasma from said ion generating feed gas to form ions;

generating a plasma from said radical generating feed gas to form radicals;

electrically biasing said substrate to a negative potential;

introducing at least one reactant gas into said deposition chamber area;

adsorbing at least one monolayer of said reactant gas on said substrate;

exposing said substrate to said ions and said radicals;

modulating said ions; and

reacting said adsorbed monolayer of said reactant gas with said ions and said radicals to deposit said thin film.

29. The method of claim 28, further comprising exposing said substrate to at least one additional reactant gas.

30. The method of claim 28, further comprising exposing said substrate to said reactant gas while varying exposure of said substrate to said ions via said ion modulation.

31. The method of claim 30, wherein said ion modulation is effected in a way selected from the group consisting of modulating an ion flux and modulating an ion energy.

32. The method of claim 31, wherein modulation in said ion flux is modulated in a way selected from the group consisting of modulating a flow of said ion generating feed gas, modulating a power of said plasma, mechanically occluding said ions, and modulating the relative movement between said plasma and said substrate.

33. The method of claim 28, further comprising maintaining said substrate at a temperature of between about 25 °C to 350 °C.

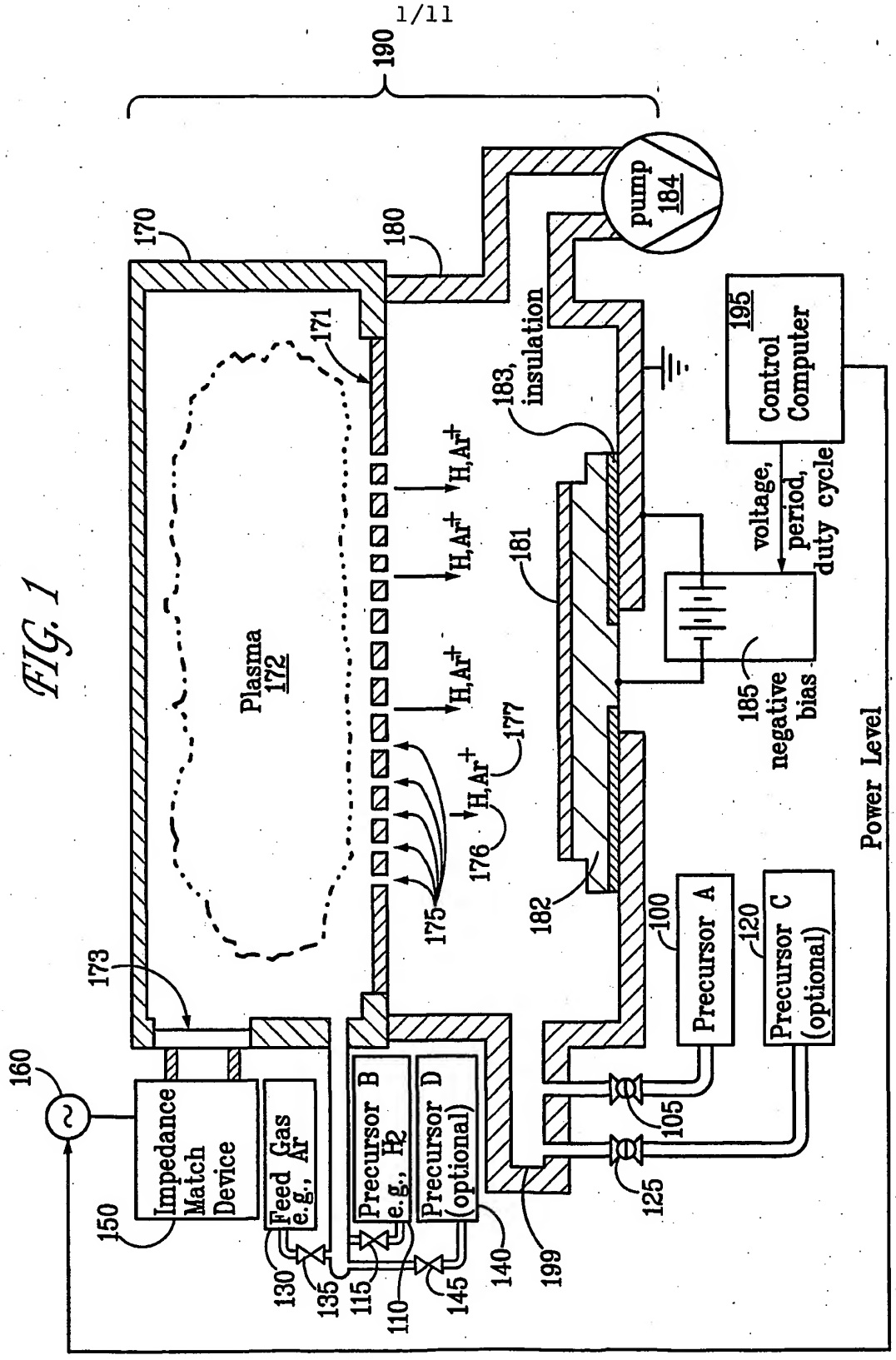
190
pump 184
170
180
171
Plasma 172
183, insulation
195 Control Computer
voltage, period, duty cycle
181
185 negative bias
177
176
175
182
100 Precursor A
120 Precursor C (optional)
Power Level
173
160
150 Impedance Match Device
Feed Gas e.g., Ar
Precursor B e.g., H2
Precursor D (optional)
130
135
115
110
145
140
199
105
125

FIG. 1

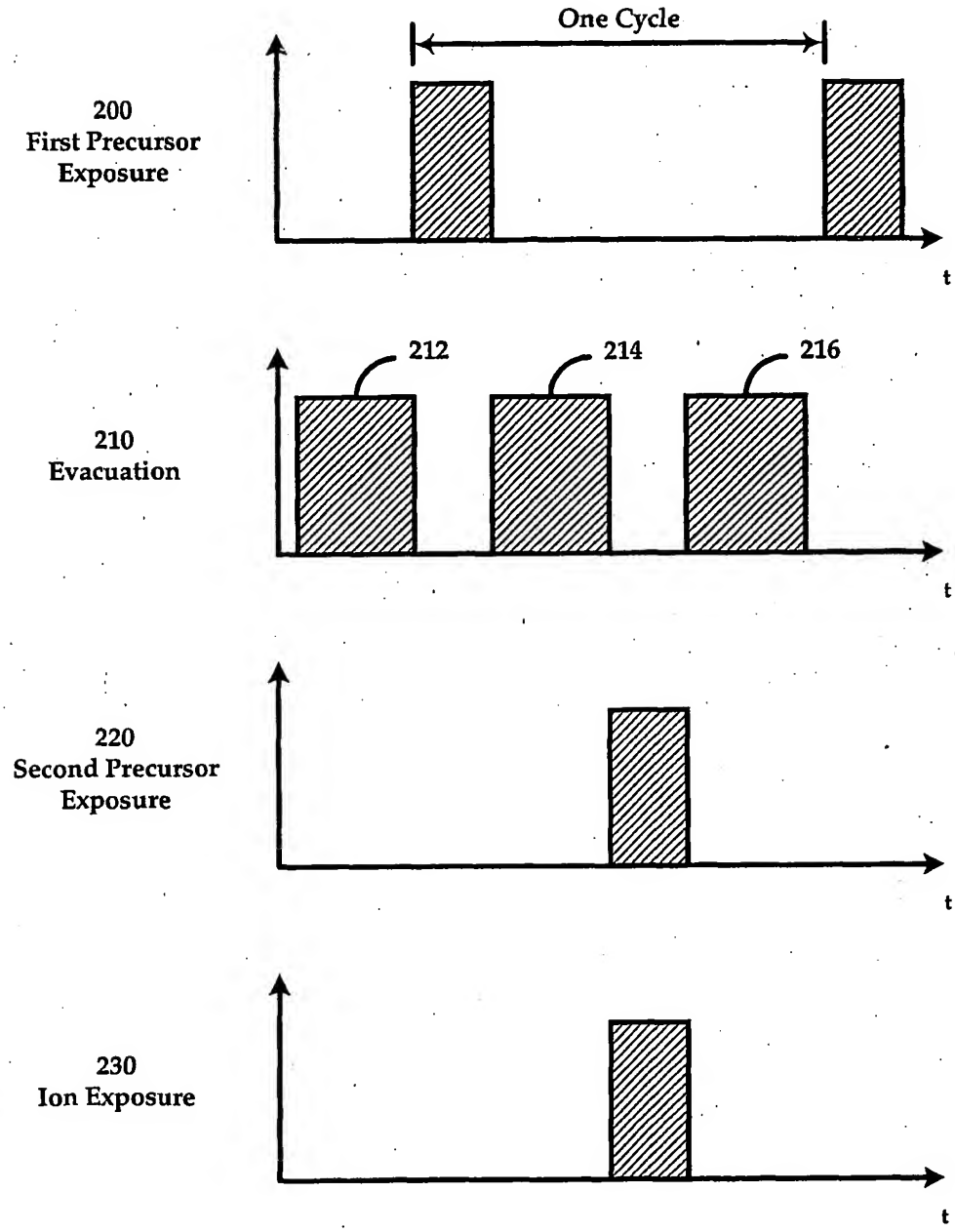
One Cycle
200
First Precursor
Exposure
t
212
214
216
210
Evacuation
t
220
Second Precursor
Exposure
t
230
Ion Exposure
t

Figure 2A

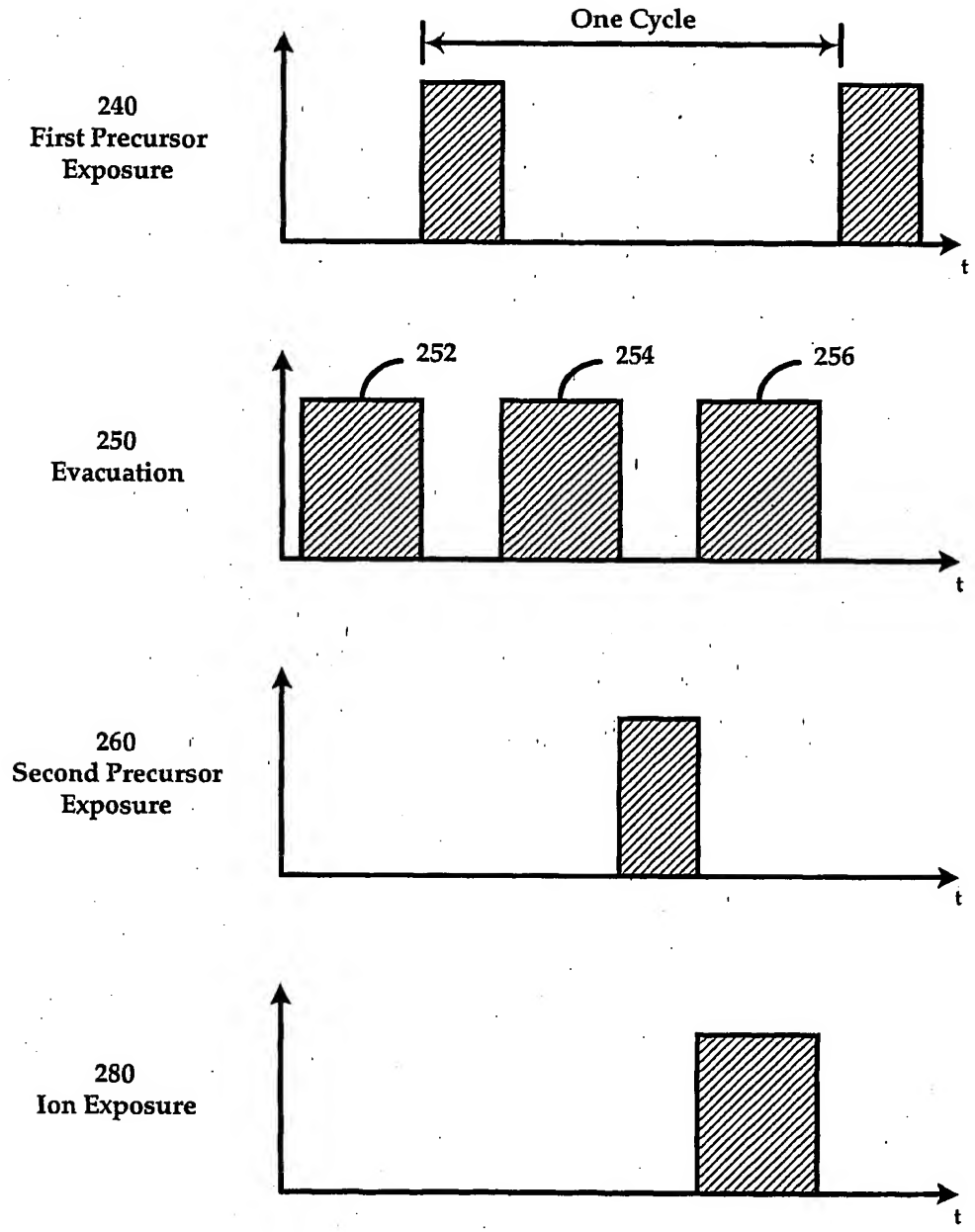
One Cycle
240
First Precursor
Exposure
t
252
254
256
250
Evacuation
t
260
Second Precursor
Exposure
t
280
Ion Exposure
t

Figure 2B

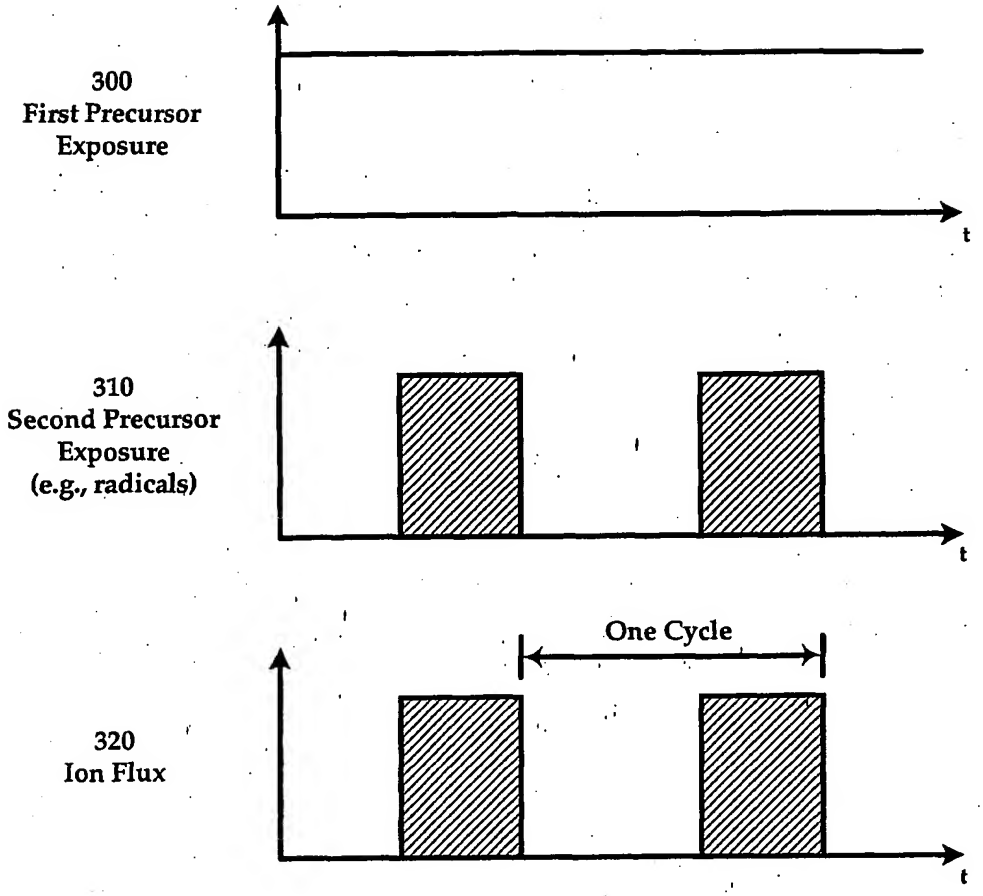
300
First Precursor
Exposure
t
310
Second Precursor
Exposure
(e.g., radicals)
t
One Cycle
320
Ion Flux
t

Figure 3A

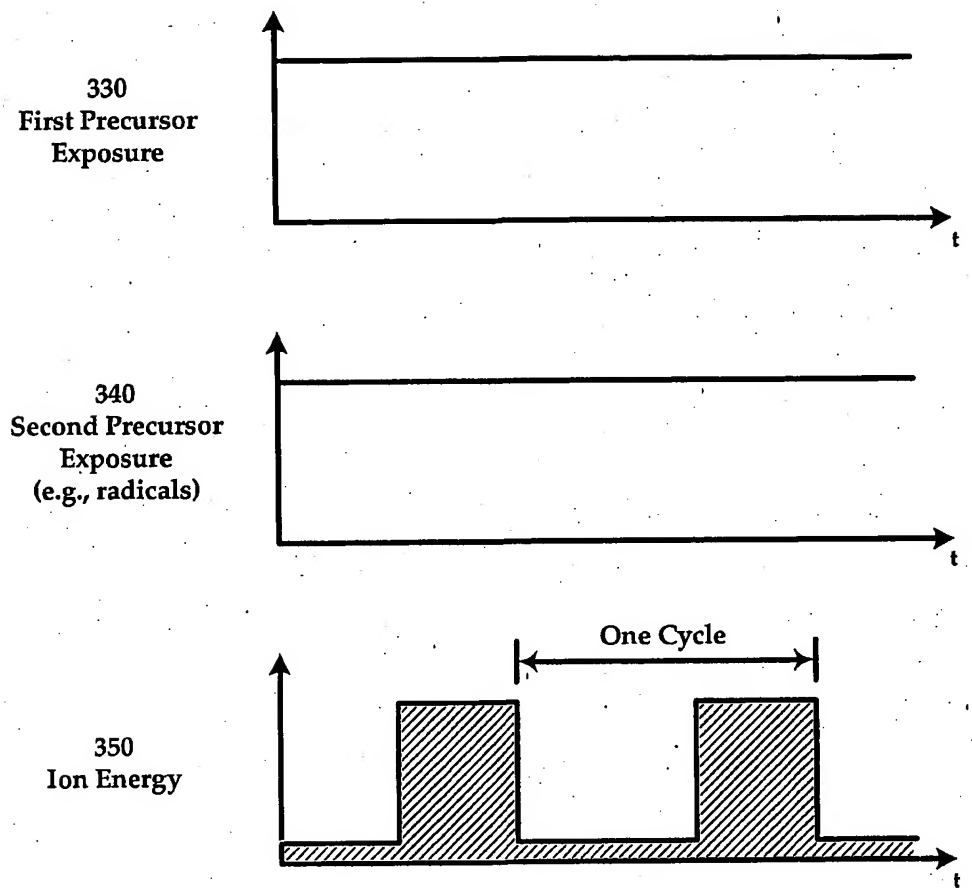
330
First Precursor
Exposure
t
340
Second Precursor
Exposure
(e.g., radicals)
t
One Cycle
350
Ion Energy
t

Figure 3B

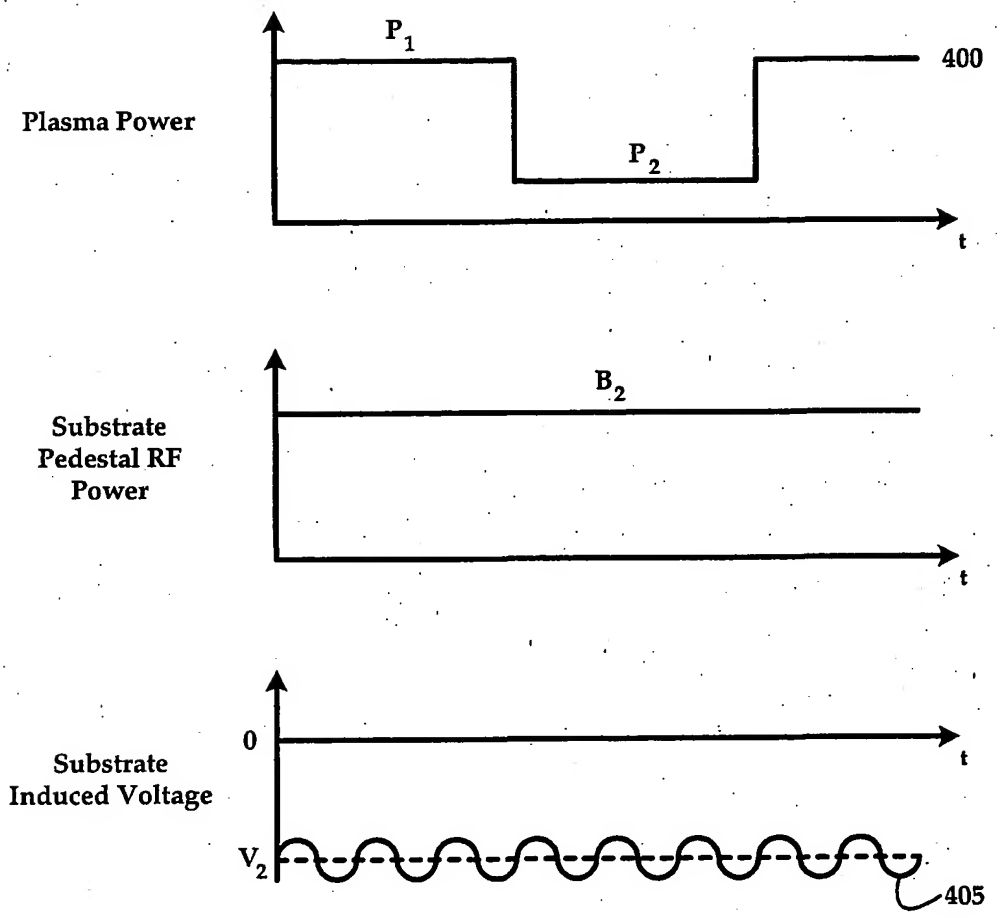
Plasma Power
P1
P2
400
t
Substrate Pedestal RF Power
B2
t
Substrate Induced Voltage
0
t
V2
405

Figure 4A

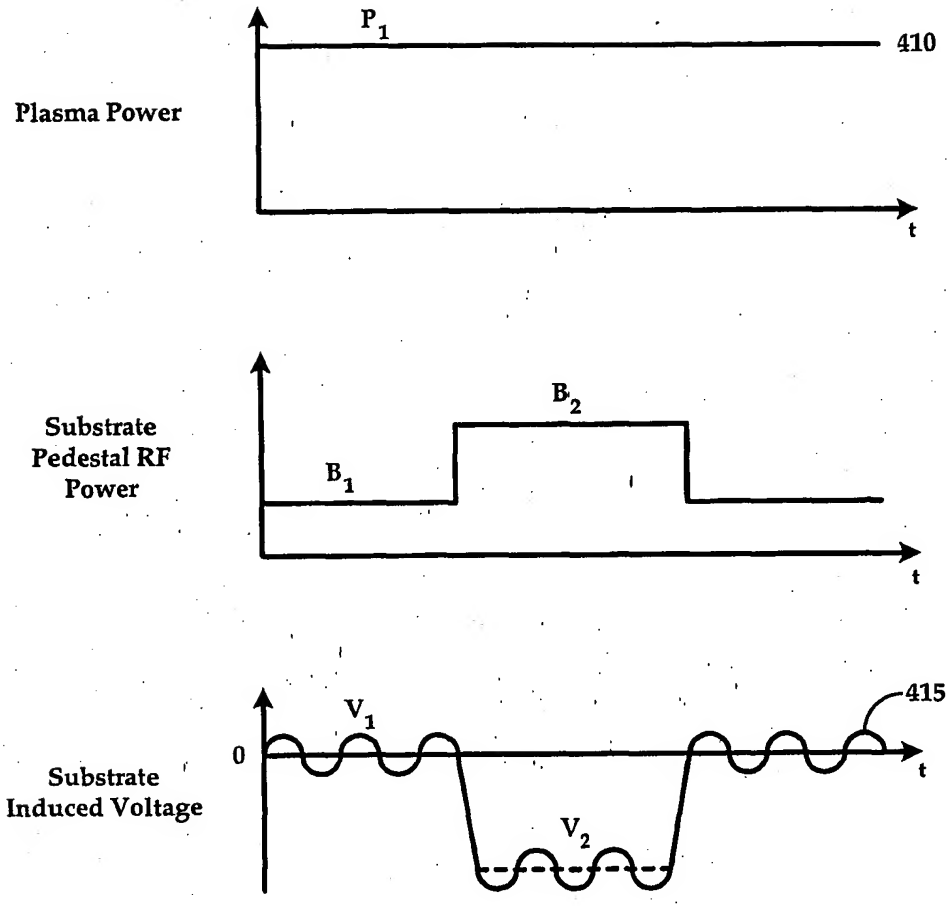
Plasma Power
P1
410
t
Substrate Pedestal RF Power
B2
B1
t
Substrate Induced Voltage
0
V1
V2
415
t

Figure 4B

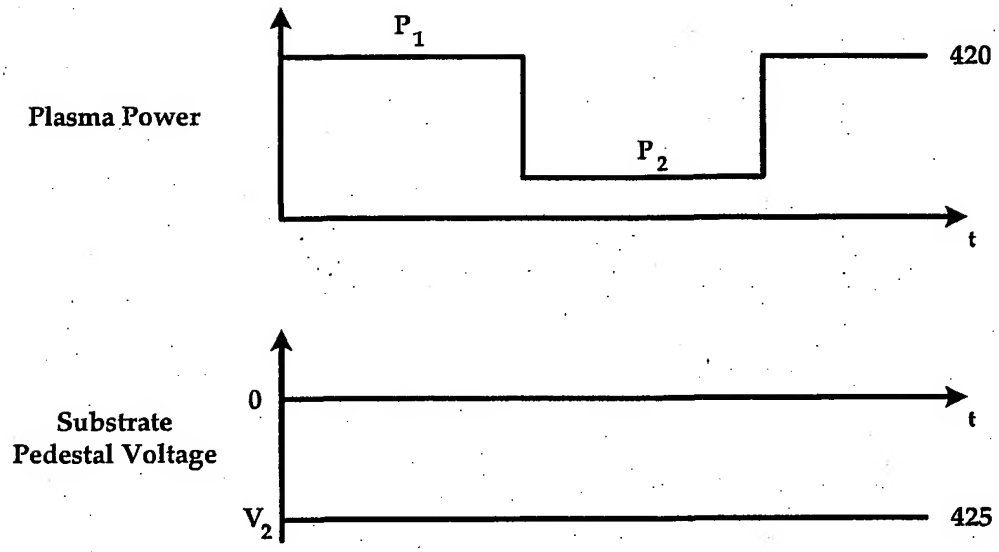

Figure 4C

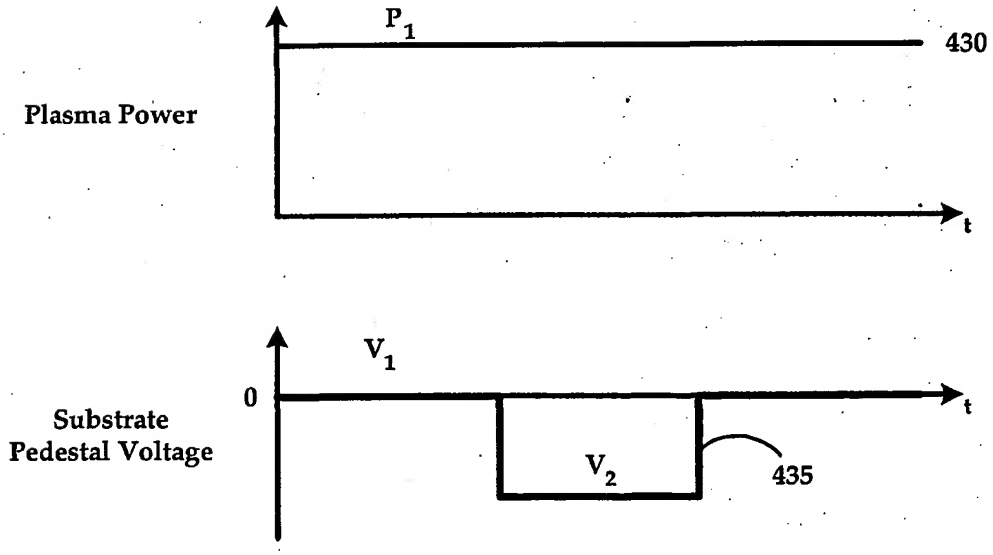

Figure 4D

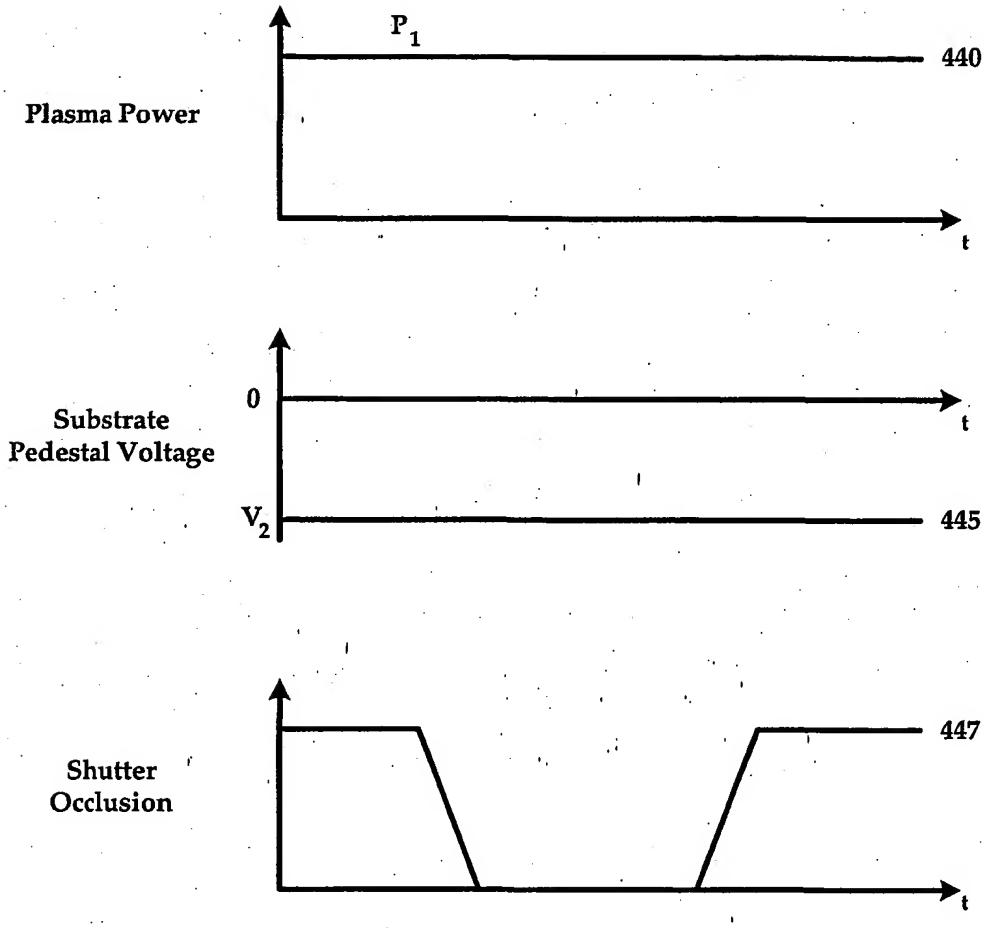
Plasma Power
P_1
440
t
Substrate
Pedestal Voltage
0
t
V_2
445
Shutter
Occlusion
447
t

Figure 4E

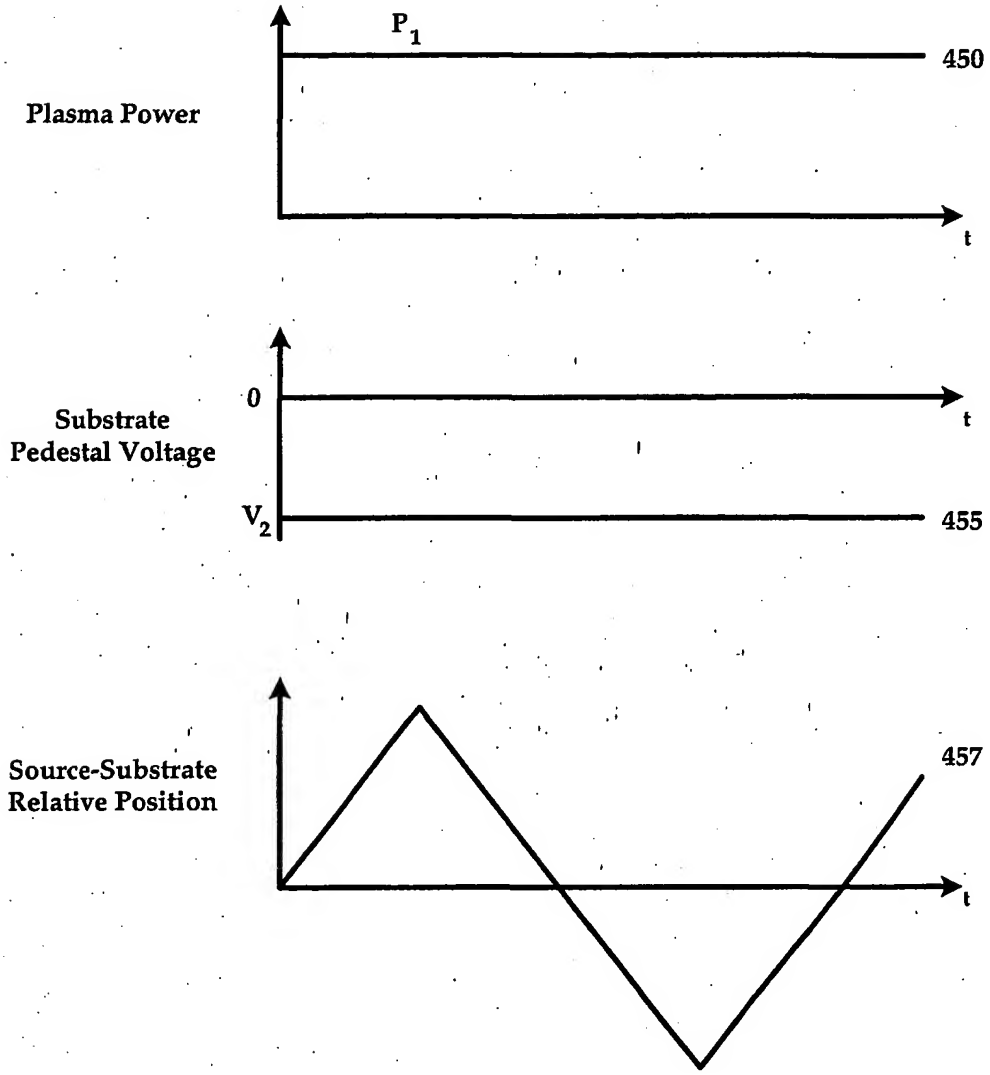
Plasma Power
P_1
450
t
Substrate
Pedestal Voltage
0
t
V_2
455
Source-Substrate
Relative Position
457
t

Figure 4F

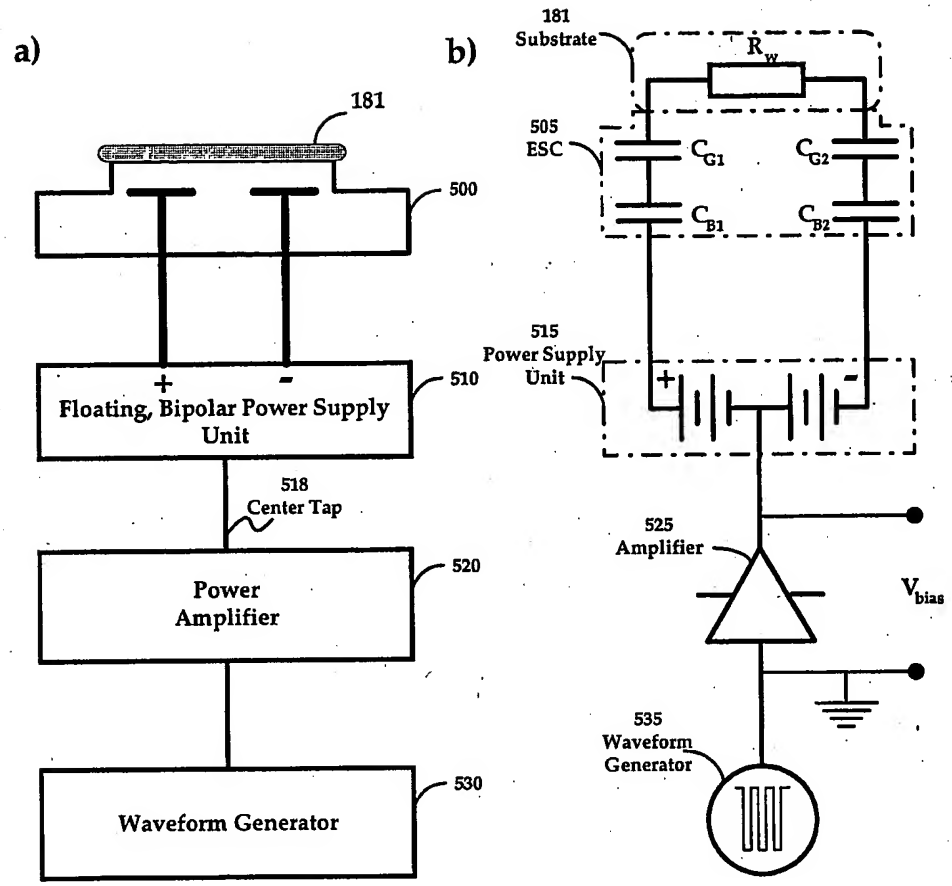
a)
181
500
+
-
Floating, Bipolar Power Supply Unit
510
518
Center Tap
Power Amplifier
520
Waveform Generator
530
b)
181
Substrate
R_w
505
ESC
C_{G1}
C_{G2}
C_{B1}
C_{B2}
515
Power Supply Unit
+
-
525
Amplifier
V_{bias}
535
Waveform Generator

Figure 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/50350

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B05D 3/04; C23C 16/00, 16/44, 16/452, 16/455, 16/505, 16/511; C30B 25/00, 25/08, 25/14; H05H 1/24

US CL : 427/561, 569, 570, 575. 248.1, 255.28, 255.5; 117/88, 92, 103, 105; 118/719, 723R, 723MW, 723I, 729

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Continuation Sheet

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,916,365 A (SHERMAN) 29 June 1999 (29.06.1999), abstract, figures 1-3, columns 5-6, and column 7, lines 13-26.	1-3, 16-22, 26 --- 23-25, 27
X,P --- Y,P	US 6,200,893 B1 (SNEH) 13 March 2001 (13.03.2001), abstract, figure 1, columns 3-6, column 7, lines 1-25, column 8, lines 5-15, column 10, lines 35-67, and column 11, lines 1-11.	1, 2, 16-21 --- 3, 22-27
X --- Y	US 4,401,054 A (MATSUO et al) 30 August 1983 (30.08.1983), abstract, figures 3 and 6, columns 5-7, column 8, lines 1-5, column 9, lines 39-56, column 10, lines 20-65, columns 11-12, column 14, lines 60-67, and column 15, lines 1-3 and 36-38.	4, 7-15 --- 5, 6, 23-25
Y	US 5,762,714 A (MOHN et al) 09 June 1998 (09.06.1998), column 2, lines 8-17.	24
Y	US 5,478,403 A (SHINAGAWA et al) 26 December 1995 (26.12.1995), column 7, lines 20-24.	5, 6, 27

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

11 March 2002 (11.03.2002)

Date of mailing of the international search report

04 APR 2002

Name and mailing address of the ISA/US

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Box PCT
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Shrive Beck

Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/50350

Continuation of B. FIELDS SEARCHED Item 1:
427/532, 533, 535, 561, 562, 564, 569, 570, 573, 575, 248.1, 250, 255.23, 255.28, 255.5; 117/84, 88, 89, 91, 92, 93, 98, 99, 100, 103, 105; 118/715, 719, 723R, 723MW, 723ME, 723I, 723IR, 728, 729

Continuation of B. FIELDS SEARCHED Item 3:
WEST electronic search, all databases.
search terms: ALD, ALE, atomic layer deposition, atomic layer epitaxy, plasma, ion, radical, showerhead, sequential CVD, and various combinations thereof.